

*The Absorption of Light by Elements in the State of Vapour :
Selenium and Tellurium ; Mercury, Zinc, Cadmium ; Phosphorus, Arsenic, Antimony.*

By Sir J. J. DOBBIE, F.R.S., and J. J. FOX, O.B.E., D.Sc.

(Received June 10, 1920.)

[PLATES 1-3.]

Apart from what can be learned from the study of their density, little is known as to the constitution in the state of vapour of those elements which are solid or liquid at ordinary temperatures. In a paper read before the Society early last year* we showed that interesting information on this subject can be obtained from the examination of the absorption spectra of sulphur. In the present paper we propose to give an account of the application of the method to other elements. Unfortunately, the number of elements which lend themselves to the purpose is small, being limited to those which do not attack silica at a high temperature and volatilise below 1300° – 1400° C., the temperature at which silica begins to soften. Those most suitable for examination, besides the members of the sulphur group, are the mercury group, comprising mercury, zinc, and cadmium, in which the molecules are known to be mainly monatomic at all temperatures above their boiling points, and the phosphorus group, comprising phosphorus, arsenic, and antimony, in which the molecules are tetratomic.

The apparatus and arrangements employed in the investigation were similar to those described in the paper on sulphur, except that the tubes were exhausted as completely as possible by the Sprengel pump.

Selenium and Tellurium.

The general character of the absorption exercised by selenium is shown in fig. 1. From an examination of this figure, it will be seen that there is an increase in the amount of the absorption from 510° C. up to about 650° C., from which point it diminishes up to 850° C. Above 850° C., no further change is observed even at the highest temperature reached in our experiments, viz., 1350° C. These changes in the absorption spectrum can be followed readily by the changes of colour observed when the light, after passing through the vapour, is allowed to fall upon a white screen. The vapour is seen to become pale yellow almost suddenly at 600° C.; between 600° C. and 700° C. it is deep orange, and at this temperature it is almost

* 'Roy. Soc. Proc.,' A, vol. 95, p. 484 (1919).

opaque to the rays of the Nernst lamp. About 850°C. the colour has again become pale yellow, and no further change takes place at higher temperatures. A remarkable feature of these changes is the narrow range of temperature within which they occur.

The spectrum of selenium shows many narrow and sharp absorption bands, and presents generally the same channelled character as the spectrum of sulphur.

From the boiling point up to 900°C. the density of selenium vapour diminishes. At this temperature it corresponds closely with the formula Se_2 , and, according to Biltz,* this is still the molecular constitution at 1800°C. This agrees with our observation that there is no change in the absorption between 850°C. and 1350°C. According to Preuner and Brockmüller,† who deduced the molecular complexity from measurements of the vapour pressure carried out with a spiral quartz manometer, the selenium molecule approaches Se_6 at the lowest temperature of their observations, and Se_2 at the highest. At intermediate temperatures, intermediate values were obtained, the larger molecules, Se_6 , appearing to break down gradually into the smaller molecules, Se_2 . The vapour densities, which have been observed below 900°C. , are all greater than are required by the formula Se_2 . Determinations have been made by Szarvasy‡ at 918°C. , 898°C. , 815°C. , and 774°C. , at which the densities referred to air were found to be 5.60, 5.83, 6.63, and 7.01 respectively. When these results are plotted out, they are seen to lie on a straight line, which, when produced (see fig. 2), gives at 700°C. a density of 7.7, and at 650°C. a density of 8.2, the latter corresponding exactly with Se_3 .

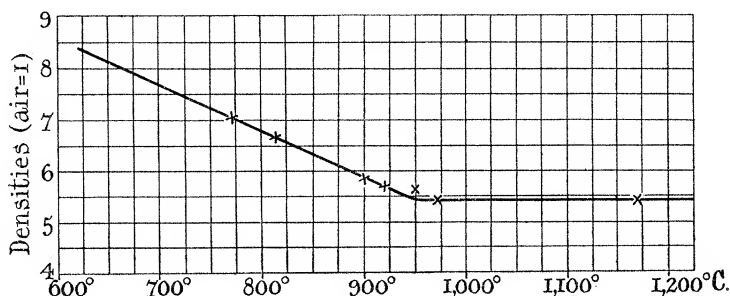


FIG. 2.

This temperature is very near the temperature of maximum absorption, which, as will be seen from the photograph (fig. 1), lies in the region of

* 'Zeit. physikal. Chem.,' vol. 19, p. 415 (1896).

† 'Zeit. physikal. Chem.,' vol. 81, p. 129 (1912).

‡ 'Ber. Deut. Chem. Ges.,' vol. 30, p. 1244 (1897).

650° C. to 700° C. There is thus close correspondence between the absorption curve and the vapour density curve so far as the data allow of the comparison being made. The point of maximum absorption of selenium lies very near that of sulphur, viz., 650° C., and strangely enough, as in the case of sulphur, the vapour density at that temperature corresponds with an average value of 3 atoms per molecule. It is also remarkable that both elements become wholly diatomic about 900° C.

The behaviour of tellurium is very similar to that of selenium, but owing to its much higher point of volatilisation, observations could be made only over a comparatively short range of temperature. From fig. 3 it will be seen that the general absorption increases with rise of temperature up to about 1250° C., after which it diminishes up to 1350° C. The light transmitted, which is pale yellow at the lower temperatures at which observations were made, becomes deep red at 1250° C., and again pale yellow at 1350° C. The spectrum is channelled like that of selenium. The only recorded vapour densities of tellurium were made at high temperatures. According to Biltz* the density at 1750°–1800° C. is 9.13, a value which corresponds nearly with the formula Te_2 . At high temperatures, therefore, the vapour of tellurium is undoubtedly composed mainly, if not entirely, of diatomic molecules, but in view of its similarity in behaviour to sulphur and selenium as regards the absorption of light, it may with great probability be inferred that, as in the case of these elements, its molecules are more complex at 1250° C. and lower temperatures than at 1750° C. At 1250° C. the constitution of its vapour would appear to be analogous to that of sulphur and selenium at 650° C.

On examining the photographs showing the absorption phenomena of the three elements of the sulphur group, it is seen that in order to obtain comparable results, the greater the atomic weight, the smaller is the quantity of the element that must be employed. In other words, the power of absorption increases with the atomic weight, and this we shall show in a future paper holds good also for the chlorine group.† With 8 mgrm. of tellurium the whole of the visible spectrum is cut out under the conditions of our experiments, whereas in the case of sulphur this is a very convenient quantity to employ in studying the absorption spectrum.

The following is a list of the principal absorption bands observed with the vapours of selenium and tellurium throughout the whole range of temperature employed:—

Selenium.— λ 5368*f*, 5299*f*, 5158*f*, 5136*w*, 4988*w*, 4972*w*, 4906, 4885*w*,

* 'Ber. Berlin Akad.,' p. 63 (1896).

† See also Mrs. Laird, 'Astrophys. J.,' vol. 14, p. 85 (1901).

4867*f*, 4844, 4815*w*, 4806, 4793, 4756*f*, 4726*w*, 4703, 4693, 4668, 4655, 4637, 4614*f*, 4590, 4557, 4528, 4504*w*, 4484, 4465, 4435, 4349*f*, 4304*f*, 4281*f*, 4242*f*, 4192*f*, 4179*f*, 4158, 4131, 4109, 4089, 4072, 4051, 4025, 4010*f*, 3988, 3976, 3955, 3937, 3920, 3899, 3878, 3868, 3841, 3834, 3820, 3810, 3790, 3778, 3765, 3755, 3743, 3734, 3723, 3712, 3703, 3690, 3678, 3667, 3655, 3627*f*.

The bands from λ 4435 to the red end of the spectrum are those of Se_2 since these occur at 900°C . and higher, at which temperatures selenium vapour is diatomic.

Tellurium.— λ 6331, 6316, 6284, 6259, 6220, 6201, 6180*w*, 6135*w*, 6115*w*, 6077*w*, 6046*w*, 6026, 6015*w*, 5968, 5951*w*, 5931, 5921, 5912, 5884, 5853*w*, 5830, 5797*w*, 5761*w*, 5748*w*, 5710*w*, 5701, 5689*w*, 5672, 5656*w*, 5639, 5624, 5614, 5581, 5565, 5550, 5528, 5504, 5489, 5466, 5451, 5439, 5426, 5415, 5399, 5389, 5369, 5358, 5347, 5329, 5316, 5308, 5295*w*, 5288, 5280, 5271, 5259, 5244, 5218, 5210, 5204, 5192, 5180, 5171, 5150, 5135, 5121, 5110, 5103, 5089, 5079, 5058, 5049, 5038, 5026, 5015, 5005, 4995, 4985, 4974, 4965*w*, 4956, 4947, 4937, 4926, 4901, 4888, 4879, 4863, 4844, 4834, 4817, 4802, 4794, 4783, 4774, 4760, 4745, 4735, 4723, 4716, 4709, 4698, 4687, 4675, 4664, 4646, 4639, 4629, 4619, 4602, 4590, 4578, 4568, 4559, 4546, 4537, 4526, 4519, 4512, 4505, 4498, 4491, 4485, 4478, 4469, 4459, 4451, 4440, 4428, 4419, 4411, 4400, 4391, 4380, 4373, 4367, 4360, 4348, 4340, 4330, 4321, 4312, 4303, 4294, 4284, 4275, 4266, 4256, 4246, 4236, 4227, 4220, 4211, 4204, 4190, 4179, 4162, 4142, 4134, 4114, 4106, 4086, 4062, 4041, 4024, 4018, 4006*w*, 3996, 3981, 3962, 3945, 3931, 3924, 3910, 3893, 3878, 3865, 3851, 3837, 3825.

The band at λ 4006 is the widest of this series of tellurium bands. Tellurium also exhibits a very wide area of absorption, the middle of which occurs about λ 4000 (fig. 4).

In the above list, *f* denotes a faint band, and *w* a wide band, the values shown in the latter case being the centre of the bands, which as a rule were of unequal sharpness at the edges.

Mercury, Zinc, Cadmium.

With a tube 100 mm. long and 12.5 mm. internal diameter containing 25.6 mgrm. of the metal, mercury showed no absorption at any temperature, the whole of the spectrum of the Nernst filament, which reaches to about λ 3100, being transmitted unaltered; with 46.6 mgrm. there was a slight absorption extending to about λ 3200, but very little further increase in absorption was observed when a tube 200 mm. long containing 105.8 mgrm.

was employed. The results were the same at all temperatures between 370°C . and 1300°C .

Cadmium (figs. 5 and 6), like mercury, shows no general absorption at any temperature, even with so large a quantity as 22.2 mgrm., but a small number of sharply defined absorption bands occur in the ultra-violet region of the spectrum in the following positions:—(a) A very fine sharp band at $\lambda 3793$, which shows at a temperature of 900°C . (b) A fine band at $\lambda 3260$ or $\lambda 3261$, showing first about 600°C ., which widens as the temperature is raised; the widened band is sharp towards the red end, but shades off towards the ultra-violet. It coincides in position with the strong line of the cadmium arc at $\lambda 3261.1$. (c) A diffuse band at $\lambda 3186$, showing first at 900°C . (d)* Two sharp bands at $\lambda 3654$ and $\lambda 3699$, showing first about 1200°C . (e)* $\lambda 3061$, appearing at 1000°C ., and $\lambda 3382$, appearing at 1100°C .

As it seemed possible that some of these bands might be due to impurities, great pains were taken to obtain the metal in the highest state of purity. Samples from American and German sources and samples prepared in the Government Laboratory by electrolytic deposition from acid solutions were all found to give identical results, and we conclude, therefore, that the bands are those of cadmium and are not due to impurities.

Zinc behaves generally in the same way as mercury; with 17.8 mgrm. no general absorption was observed at any temperature between that of volatilisation and 1300°C . At 1100°C . four very sharp faint bands make their appearance at $\lambda 3699$, $\lambda 3654$, $\lambda 3384$, and $\lambda 3284$. The zinc employed was the purest that could be obtained, and was free, so far as chemical tests showed, from all other metals except traces of lead and cadmium amounting to 0.016 per cent. and 0.005 per cent. respectively. Such minute quantities are, so far as our experience goes, without effect on the absorption spectra.

Considered as a group, these elements differ widely from sulphur and resemble each other in that: (1) they are transparent to light as far as the spectrum of the Nernst filament extends, that is, to about $\lambda 3100$; (2) increase of temperature is not accompanied by the peculiar behaviour exhibited by sulphur, viz., increase of absorption followed by decrease as the temperature is raised; (3) increase in the quantity of the element within the limits of our experiments has little influence upon the spectrum. The results obtained with 46.6 mgrm. of mercury are much the same as with more than double that quantity; with 10.4 mgrm. of cadmium the same as with 22.2 mgrm., and with 17.8 mgrm. of zinc the same as with 28.4 mgrm.

* These lines are not shown in the reproduction, although clearly marked on the original negatives.

Phosphorus, Arsenic, Antimony.

Phosphorus, arsenic, and antimony, which are known from their vapour densities to be tetratomic, behave differently from the elements of the other groups already examined. With 9.4 mgrm. of phosphorus heated from 420° C. to 1310° C. the spectrum, which extends to λ 3300 at the lower temperature, gradually contracts as the temperature is raised, until at the highest temperature reached it only extends to λ 3730. With 13.6 mgrm. the result is similar, the only difference being that the amount of absorption is greater, the spectrum only reaching to λ 3400 at 420° C. and to λ 3950 at 1310° C. The phosphorus, it may be mentioned, was introduced into the tube in the red or amorphous form.

Arsenic shows similar phenomena to phosphorus. Between 400° C. and 1320° C. (fig. 7) there is a regular increase in the general absorption, the spectrum being transmitted to λ 3250 at 400° C. and to λ 4440 at 1320° C. When the amount of arsenic is increased, the only effect is to increase the amount of absorption at corresponding temperatures. The absorption extends in this case into the visible region of the spectrum and the colour of the arsenic vapour becomes faintly yellow at 700° C., deepening as the temperature is raised.

On account of the higher temperature required to volatilise antimony, this element could only be examined over a comparatively short range of temperature, viz., 800° C.–1300° C., but it will be seen from fig. 8 that between these temperatures it behaves in the same way as phosphorus and arsenic. With 31.6 mgrm. the spectrum is transmitted to λ 3150 at 800° C. and to λ 4000 at 1300° C. The antimony used was prepared from tartar emetic.

It may here be mentioned that in dealing with elements which require a high temperature for volatilisation it is found most convenient to heat the tube to the highest temperature to begin with, and take the photographs as the temperature falls, so as to ensure that the whole of the contents of the tube are in the state of vapour during examination. The deposition of any of the elements in the solid state is at once indicated by the light being partially or entirely cut off by obscuration of the end plates.

It is well known that the density of the vapour of phosphorus, arsenic, and antimony diminishes with increase of temperature. It may, therefore, be assumed that, as in the case of sulphur, the increase of absorption which takes place when the temperature is raised is closely associated with the breaking down of the more complex molecules. No absorption bands or indications of any kind of selective absorption were observed in the elements of this group.

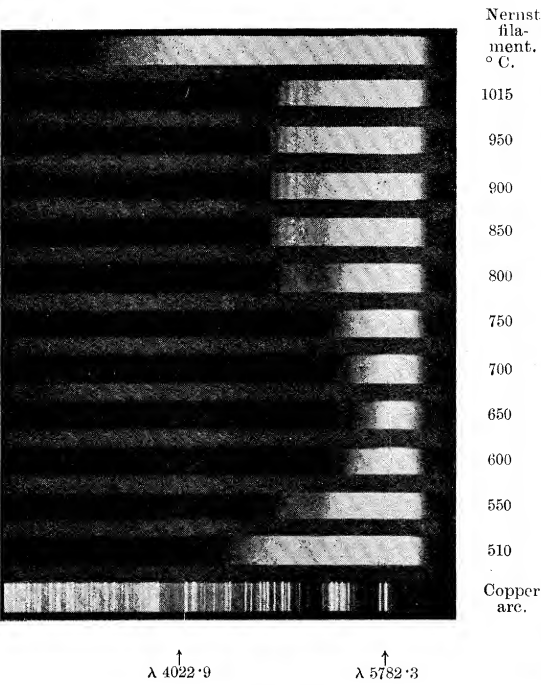


FIG. 1.—Spectrum of 4.3 mgrm. of Selenium.

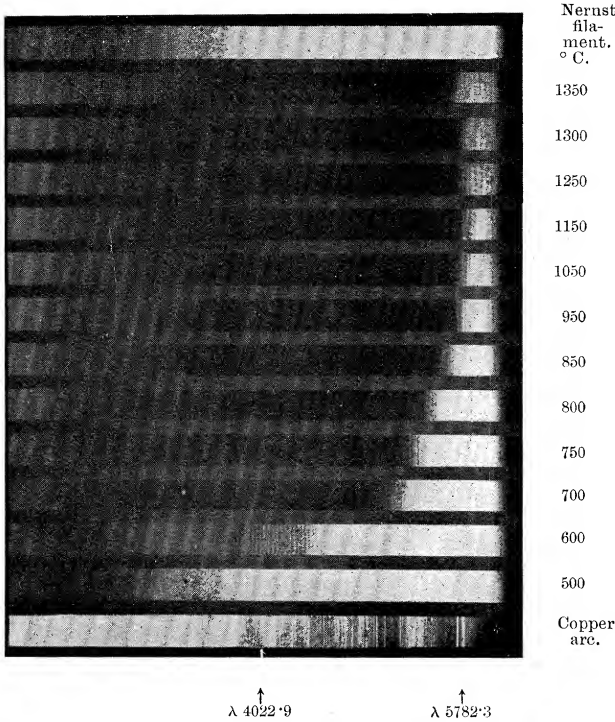


FIG. 3.—Spectrum of 4.9 mgrm. of Tellurium.

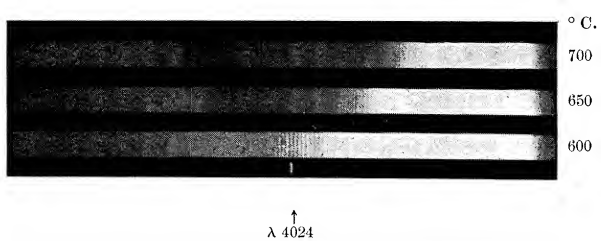


FIG. 4.—Spectrum of 0.4 mgrm. of Tellurium.

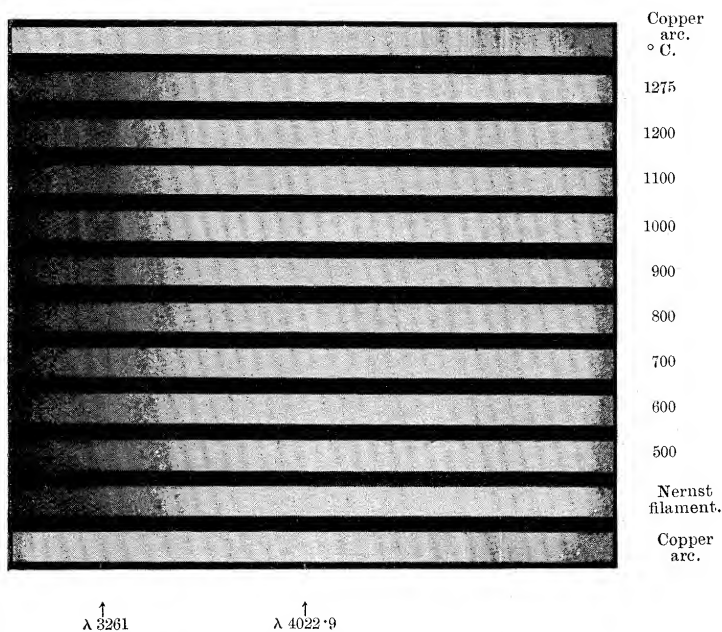


FIG. 5.—Spectrum of 22.2 mgrm. of Cadmium.

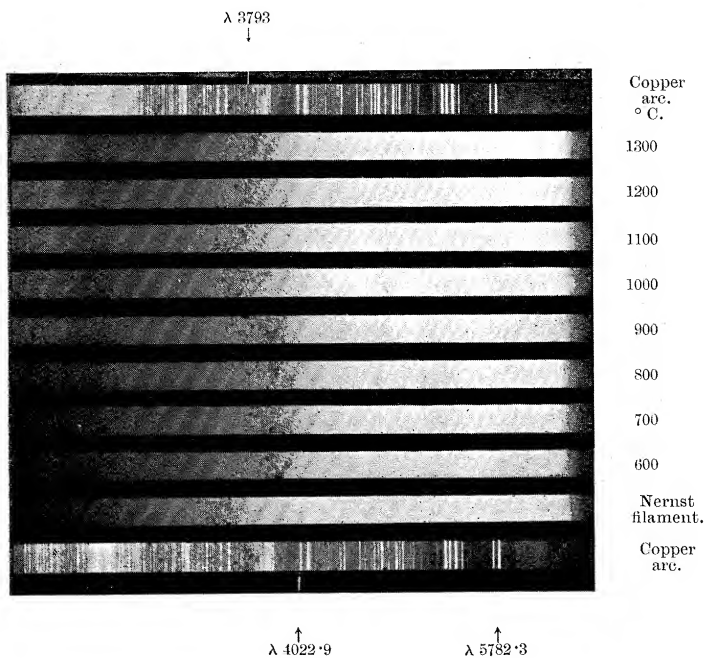


FIG. 6.—Spectrum of 21.6 mgrm. of Cadmium.

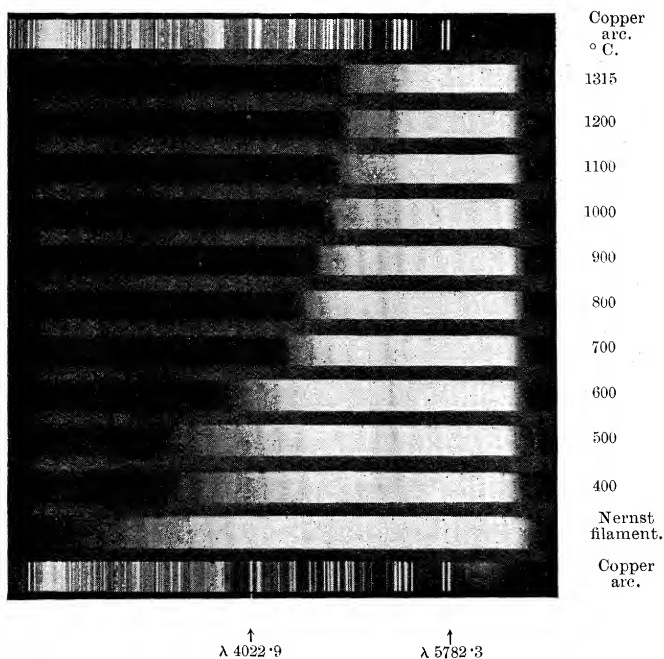


FIG. 7.—Spectrum of 24.6 mgrm. of Arsenic.

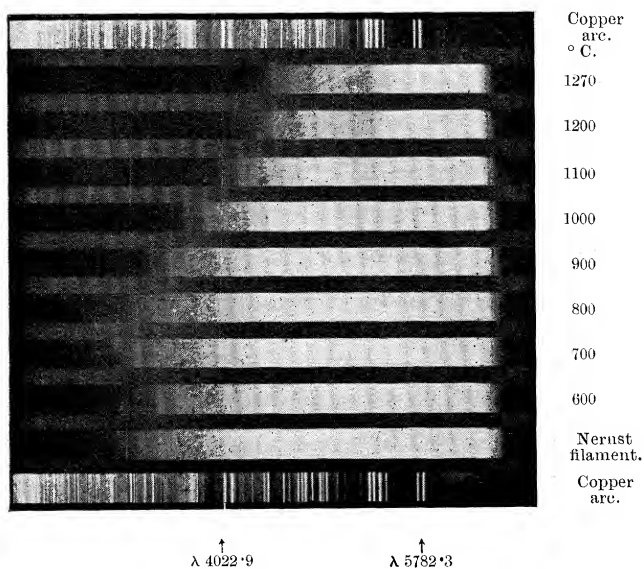


FIG. 8.—Spectrum of 31.6 mgrm. of Antimony.

Where the absorption of light increases with increase of temperature there is evidence of the resolution of more complex into simpler molecules; where there is no increase of absorption there is evidence that the element is monatomic in the gaseous state. In the case of mercury the evidence, based on several distinct methods of investigation, points to the conclusion that the vapour consists entirely of molecules composed of single atoms. The vapours of zinc and cadmium have densities which indicate that their molecules also for the most part consist of single atoms. The discrepancy, however, between the vapour density, calculated on the assumption that these two elements are monatomic, and that actually observed even at high temperature shows that the molecules in the gaseous state do not *wholly* consist of single atoms. The fine bands described above may well be connected with the presence of the more complicated molecules.

Bearing in mind the results previously obtained with sulphur, it would appear that the elements which lend themselves to examination by the method described in this paper may be divided into three groups:—

(1) Elements whose vapours exercise no absorption or show only a few well-defined absorption bands: these are monatomic.

(2) Elements in which the absorption gradually increases as the temperature is raised, but which show no other effect within the limits of temperature imposed by our method: these are tetratomic.

(3) Elements in which the absorption increases with increase of temperature to a maximum and afterwards diminishes. The sulphur and halogen elements belong to this group.

The explanation of the different behaviour as regards absorption of light, as exhibited by elements of groups (2) and (3) compared with those of group (1), is probably to be found in the rearrangement of the valencies accompanying the breaking down of the complex molecules under the action of heat. The tetratomic molecules would appear to break down simply into diatomic molecules, although possibly more complicated changes may take place at higher temperatures than can be employed with silica tubes. With the sulphur and halogen elements, the changes are obviously much more complex. The molecules near the temperature of volatilisation are probably already broken down, partially to the atomic condition, the liberated atoms forming new combinations with one another or with the undissociated molecules, in other words, polymerising. This subject will be more fully discussed in a future communication on the elements of the halogen group, which we are at present investigating.

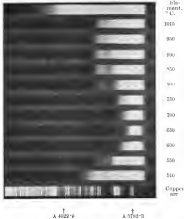


FIG. 1.—Spectrum of 43 mgm. of Selenium.

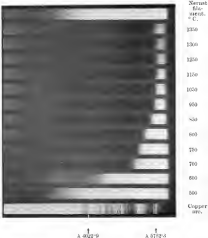
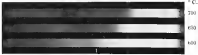


FIG. 3.—Spectrum of 4.9 mgm. of Tellurium.



†
A 1021

FIG. 4.—Spectrum of 0.4 mgm. of Tellurium.

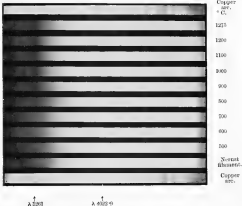


FIG. 5.—Spectrum of 23.2 mgrm. of Cadmium.

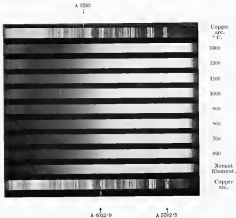


FIG. 6.—Spectrum of 21.6 mgrm. of Cadmium.

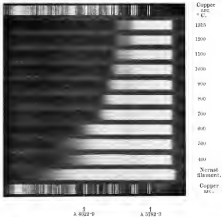


FIG. 7.—Spectrum of 246 mgm. of Arsenic.

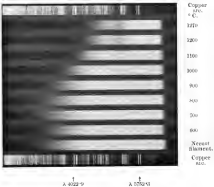


FIG. 8.—Spectrum of 31.6 mgrm. of Antimony.